MEASURING THE THERMODYNAMICS OF THE ALLOY/SCALE INTERFACE

Evan Copland
Case Western Reserve University, Cleveland, Ohio 44135

ABSTRACT

A method is proposed for the direct measurement of the thermodynamic properties of the alloy and oxide compound at the alloy/scale interface observed during steady-state oxidation. The thermodynamic properties of the alloy/scale interface define the driving force for solid-state transport in the alloy and oxide compound. Accurate knowledge of thermodynamic properties of the interface will advance our understanding of oxidation behavior. The method is based on the concept of local equilibrium and assumes that an alloy+scale equilibrium very closely approximates the alloy/scale interface observed during steady-state oxidation. The thermodynamics activities of this alloy+scale equilibrium are measured directly by Knudsen effusion-cell mass spectrometer (*KEMS*) using the vapor pressure technique. The theory and some practical considerations of this method are discussed in terms of β-NiAl oxidation.

INTRODUCTION

The use of alloys in oxygen containing atmospheres at elevated temperatures relies on the formation of a continuous oxide layer on the alloy surface that separates it from the oxidizing environment. Continued oxidation of the alloy then depends on the solid-state transport of anions and/or cations through the oxide layer. Provided the reaction rate is controlled by solid-state transport in the oxide or alloy a steady-state condition develops and the diffusion path of the reaction is independent of time (1,2). Specifically, for a given bulk alloy composition reaction temperature and oxygen pressure, the alloy/scale and scale/gas interfaces maintain constant compositions and recession of the alloy surface and oxide thickness change according to parabolic rate laws (1,2). Under steady-state conditions the oxidation behavior of some alloys can be predicted but it is a complex problem that requires a good knowledge of the transport kinetics and thermodynamic properties of both the alloy and oxide scale (3).

The thermodynamic properties of the alloy and oxide compound at the alloy/scale interface are particularly important as this interface provides the boundary condition that define the driving force for solid-state transport in both the alloy and oxide layer. To date, however, our understanding of oxidation behavior has been based on a simplified description of the alloy/scale interface in which the alloy is generally treated as ideal solution, without considering dissolved O, and oxide compounds are typically assumed to be pure with unit activity (2,3). These assumptions have proved to be very useful in the absence of accurate thermodynamic data but their continued use could limit our understanding of the more subtle, but important, aspects of oxidation behavior. This article explores this idea by proposing a method that allows the direct determination of the thermodynamic properties of the alloy/scale interface. This method is based on an extension of the concept of local equilibrium at the alloy/scale interface together with

Knudsen effusion-cell mass spectrometry (*KEMS*) to measure thermodynamic activities by the vapor pressure technique.

THE ALLOY/SCALE INTERFACE

Prior to discussing the technique for measuring the thermodynamic properties it is useful to review the features of the alloy/scale interface found during steady-state oxidation. β-NiAl is considered because Ni(g), Al(g) and Al$_2$O(g) partial pressures can be measured and it has important practical applications. Oxidation of β-NiAl in pure oxygen results in the formation and growth of an external layer of α-Al$_2$O$_3$ as shown in figure 1a. Alumina has a very limited stoichiometry range and the mole fractions of Al, $N_{Al}(Al_2O_3)_I$, and O, $N_O(Al_2O_3)_I$, can be assumed constant across the oxide thickness. There must, however, be some dissolution of Ni and α-Al$_2$O$_3$ is saturated with Ni at the alloy/scale interface, $N_{Ni}(Al_2O_3)_I$. Similarly β-NiAl has a very limited solubility of O which dissolves interstitially and the alloy is saturated at the alloy/scale interface, $N_O(\beta)_I$. In the case of β-NiAl the saturation limit of O is well below a level that has a significant effect on mechanical properties. Aluminum is selectively removed from the alloy to form α-Al$_2$O$_3$ resulting in recession of the alloy surface and a reduction in concentration from the bulk alloy composition, $N_{Al}(\beta)$, to that at the alloy/scale interface, $N_{Al}(\beta)_I$. Conversely Ni is enriched at the alloy/scale interface, $N_{Ni}(\beta)_I$, relative to the bulk alloy composition, $N_{Ni}(\beta)$.

Measured concentrations are important in defining the 'local' state of the reacting system but partial thermodynamic properties of the components are the true driving force for solid-state transport and knowledge of their variation across the reaction-zone are required to fully understand oxidation. The partial thermodynamic properties can be represented by activities, which provide a measure of the reactivity of a component in a solution phase relative to a reference state (4-6). The reference states used for activity measured in the Ni-Al-O system are defined below. This is illustrated by redrawing figure 1a in terms of approximate activities of Ni, Al, O and Al$_2$O$_3$ across the reaction-zone (see figure 1b). The relationship between composition and the thermodynamic properties is represented by the solution behavior, which can be quite complex in multi-component systems. This is particularly true for β-NiAl(O) and Al$_2$O$_3$ as both exhibit large deviations form ideal behavior. The total driving force for Al, Ni and O transport is $\left[\ln a(i)_I - \ln a(i)_o\right]$ in β-NiAl(O) and $\left[\ln a(i)_G - \ln a(i)_I\right]$ in α-Al$_2$O$_3$. This results in a flux of Al atoms to alloy/scale interface and cations out through the scale. In addition there is a flux of oxygen anions towards the alloy/scale interface and a flux of Ni and O atoms into β-NiAl(O) from the alloy/scale interface. The variation of a(Ni) through the oxide-layer is unknown but presumably there could also be a flux of Ni cations out through the scale. As the composition of the bulk alloy and vapor phase are fixed the thermodynamic properties of the alloy/scale interface (*i.e.*, a(Al)$_I$, a(Ni)$_I$, a(O)$_I$ and a(Al$_2$O$_3$)$_I$) are critical in determining the transport kinetics in β-NiAl(O) and α-Al$_2$O$_3$.

During steady-state oxidation the diffusion-path is independent of time and the composition of the alloy/scale remains fixed (7). The concentration profile shown in

figure 1a is shown schematically on an isothermal section of the condensed phase diagram of the Ni-Al-O system in figure 2 (where the solubility of O in β-NiAl(O) and Ni in α-Al$_2$O$_3$ have been exaggerated for clarity). It is typical to assume local equilibrium exists at the alloy/scale interface it can be represented by the single tie-line between β-NiAl(O)$_I$ and α-Al$_2$O$_3$ identified in figure 2. If this concept of local equilibrium is taken literally, the alloy/scale interface observed during steady-state oxidation can be very closely approximated by considering the β-NiAl(O)$_I$ + α-Al$_2$O$_3$ equilibrium.

THE KNUDSEN EFFUSION-CELL

For the scale morphology considered in figure 1, any energetic effects due directly to the interface between β-NiAl(O)$_I$ and α-Al$_2$O$_3$ (*eg*, surface tension) are assumed to be negligible compared to the bulk properties of the alloy and oxide. As a result we are free to consider a range of physical configurations for the equilibrium between β-NiAl(O)$_I$ and α-Al$_2$O$_3$. In the current case α-Al$_2$O$_3$ has the form of a 'closed' isothermal container (*Knudsen effusion-cell*) (8) that defines a small finite volume into which a small sample of β-NiAl(O)$_I$ is placed, as shown in figure 3. Apart from localized point contact, β-NiAl(O)$_I$ and α-Al$_2$O$_3$ are not in physical contact, rather both are in mutual contact with the vapor phase that fills the inner volume of the container. The vapor species (Al, Al$_2$O and Ni) result from a range of sublimation and condensation reactions involving both β-NiAl(O)$_I$ and α-Al$_2$O$_3$. At elevated temperatures (above about 1000K) the partial pressures of the vapor species and the rate of solid-state transport are significant and the 'closed' isothermal environment allows thermodynamic equilibrium between the vapor and both condensed phases to be very closely approached. Their mutual equilibrium with the vapor means that β-NiAl(O) and α-Al$_2$O$_3$ are in equilibrium in accordance with the alloy/scale interface represented by the tie-line in figure 2. The equilibrium condition means that the thermodynamic properties of each component are identical in all phases. As a result the thermodynamic properties of the equilibrium β-NiAl(O)/α-Al$_2$O$_3$ interface can be studied directly by measuring the relative partial pressure of Al(g), Al$_2$O(g) and Ni(g) in the vapor as a function of temperature.

The equilibrium vapor phase is sampled by effusion through an orifice in the effusion-cell. While effusion is a steady-state process the equilibrium condition is very closely approached and phase compositions are typically maintained during an experiment. Accurate sampling of the vapor requires molecular flow conditions are maintained and an effusion-cell design that ensures the number of atoms involved in vaporization/ condensation reactions is much greater than the number of atoms effusing from the orifice while maintaining a high transport probability to the orifice (9-12).

MULTIPLE KNUDSEN EFFUSION-CELL MASS SPECTROMETRY

Coupling an Knudsen effusion-cell vapor source to a mass spectrometer (*KEMS*) allows the simultaneous determination of the identity and pressure of the vapor species in equilibrium with β-NiAl(O) + α-Al$_2$O$_3$ as a function of temperature (13). The partial pressure of a species is determined indirectly by sampling its flux in a molecular beam (selected from the distribution of effusing molecules) by electron impact, the formation

of ions K^+ and the formation of a representative ion beam that is sorted according to mass-to-charge ratio by common mass spectrometric techniques. The partial pressure of species 'A' in the effusion-cell, $p(A)$, is related to the measured intensity of ion K^+, I_{AK}, and absolute temperature, T, by:

$$p(A) = \frac{I_{AK}T}{S_{AK}}$$ [1]

Where, S_{AK} is the instrument sensitivity factor. The measurement of absolute pressure requires the determination of S_{AK} which is a difficult problem for systems with a complex vapor phase. The traditional approach is to assume S_{AK} remains constant during an experiment and only consider relative partial pressures (i.e., $p(A) \propto I_{AK}T$).

Thermodynamic activities are defined as the ratio of a component's fugacity in a solution, β, and reference state designated by the superscript, $^\circ$, and also in terms of the change in Gibbs free energy for a mixing reaction which provides relative chemical potentials, $\mu_A^\beta - \mu_A^\circ$, as shown in equation 2 (4). At high temperatures and low pressures the vapor in equilibrium with the solution phase and reference state approach ideal behavior and the fugacity of a component can be determined by measuring the partial pressure of a characteristic vapor species, $p(A)$. Therefore the activity can be determined directly at a given temperature by comparing the partial pressure of the characteristic vapor species in equilibrium with the solution, $p(A)$, to the reference state, $p^\circ(A)$, as shown in equation 3.

$$\mu_A^\beta - \mu_A^\circ = RT \ln \frac{f}{f^\circ} = RT \ln a(A)$$ [2]

$$a(A) = \frac{p(A)}{p^\circ(A)}$$ [3]

The best approach to measuring activities with $KEMS$ is to maintain a relative nature by including multiple effusion-cells in the isothermal zone of a furnace and directly comparing the partial pressure of characteristic vapor species in equilibrium with the alloy (alloy, $p(A)$, I_{AK}) and experimental reference state (ref, $p^\circ(A)$, I_{AK}°) at one temperature (14-17).

$$a(A) = \frac{p(A)}{p^\circ(A)} = \frac{I_{AK} \cdot T}{I_{AK}^\circ \cdot T} \cdot \frac{S_{AK}(ref)}{S_{AK}(alloy)} = \frac{I_{AK}}{I_{AK}^\circ} \cdot \frac{g(ref)}{g(alloy)}$$ [4]
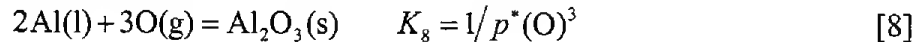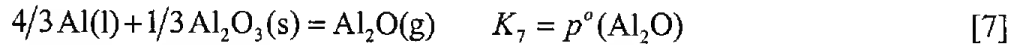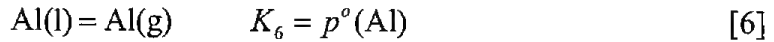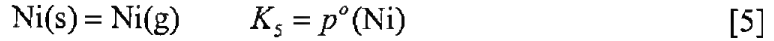
All factors in S_{AK} related to ionization and mass spectra analyses cancel, however, the geometric relation between the molecular- and electron-beam remain and is represented in equation 4 by, $g(ref)/g(alloy)$, the 'geometry factor ratio' (GFR). Provided the cells

are isothermal and molecular beam sampling is independent of the vapor source, the *GFR* for a pair of cells only depends on differences in orifice and cell shape (18).

REFERENCE STATES FOR ACTIVITY MEASUREMENTS

The measured activities of Al, Ni, O and Al_2O_3 depend on the definition of the experimental reference state. This is clear for Ni where pure-Ni(s), at the temperature of interest, is used as a reference (the typical Raoultian reference state). The reference vapor pressure, $p^o(Ni)$, is defined by the sublimation reaction [5]. For Al the stability of Al_2O_3 means Al activities cannot be measured without also considering oxygen. As a result a two phase mixture of Al(l) + α-Al_2O_3(s) at the dissociation pressure of O(g), $p^*(O)$, at the temperature of interest, is used as an experimental reference (18). This two phase mixture provides a reference state for Al, Al_2O, O, and Al_2O_3, where all are equal to unity by definition. Al_2O_3 is used as the effusion-cell material which provides a suitable container for liquid aluminum. Atomic oxygen is considered in this treatment because under these conditions it is the dominant oxygen vapor species (*i.e.*, $p(O) \gg p(O_2)$) and it is the species that dissolves in the alloy phase.

The solubility of oxygen in fcc and liquid aluminum is typically below measurement sensitivity (and less than ~0.1 at% at 2323 K) and similarly deviations of Al_2O_3 from stoichiometry are not measurable (19). For simplicity then Al(l) and α-Al_2O_3(s) can be considered to be pure substances, however, they are in reality at their saturation limits. The Al(l) + α-Al_2O_3(s) experimental reference defines the reference pressures $p^o(Al)$, $p^o(Al_2O)$ and $p^*(O)$ according to reactions 6-8.

$$Ni(s) = Ni(g) \qquad K_s = p^o(Ni) \qquad [5]$$

$$Al(l) = Al(g) \qquad K_6 = p^o(Al) \qquad [6]$$

$$4/3\,Al(l) + 1/3\,Al_2O_3(s) = Al_2O(g) \qquad K_7 = p^o(Al_2O) \qquad [7]$$

$$2Al(l) + 3O(g) = Al_2O_3(s) \qquad K_8 = 1/p^*(O)^3 \qquad [8]$$

For the β-NiAl(O) + α-Al_2O_3 equilibrium Al, Al_2O and Ni dominate the vapor and their activities are determined directly according to equation 4 where: $a(Al) = p(Al)/p^o(Al)$, $a(Al_2O) = p(Al_2O)/p^o(Al_2O)$ and $a(Ni) = p(Ni)/p^o(Ni)$. The activities of O and Al_2O_3 are determined indirectly from the measured $a(Al)$ and $a(Al_2O)$ values according to additional independent reactions in the Al-O system.

$$2Al(g) + O(g) = Al_2O(g) \qquad a^*(O) = \frac{a(Al_2O)}{a(Al)^2} \qquad [9]$$
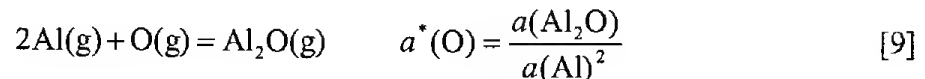
$$4\text{Al}(g) + \text{Al}_2\text{O}_3(s) = 3\text{Al}_2\text{O}(g) \qquad a(\text{Al}_2\text{O}_3) = \frac{a(\text{Al}_2\text{O})^3}{a(\text{Al})^4} \qquad [10]$$

DISCUSSION

It is important to realize that Al(l) + α-Al$_2$O$_3$(s) defines a very stable (or un-reactive) reference state for both O and Al$_2$O$_3$. Specifically $a^*(\text{O})$ is defined relative to the dissociation pressure of O(g) in equilibrium with the Al(l) + Al$_2$O$_3$(s), in terms of equation 4, $a^*(\text{O}) = p(\text{O})/p^*(\text{O})$. While this is different from the traditional reference it is very useful as its reactivity is very close to that found in the alloy/scale interface being studied which makes $a^*(\text{O})$ measurements very sensitive to alloy composition. Accordingly it is not uncommon to observe experimental oxygen activities significantly greater than unity, shown schematically in figure 1b. This simply means the density of O atoms in the vapor in equilibrium with β-NiAl(O)$_I$ + α-Al$_2$O$_3$ is greater then that in equilibrium with the reference state, $p(\text{O}) > p^*(\text{O})$. These experimental activities can be converted to more conventional values by changing the reference state of oxygen to an ideal gas, O$_2$(g), with a partial pressure of 1 bar (i.e., $a(\text{O}_2) = a^*(O)^2 \cdot K_8^{-2/3}$) (18). For Al$_2O_3$, the chemical potential is defined in terms of the chemical potentials of Al and O according to equation 11 (5,20).

$$2\mu_{\text{Al}} + 3\mu_{\text{O}} = \mu_{\text{Al}_2\text{O}_3} \qquad [11]$$

Meaningful Al$_2$O$_3$ activity measurements, therefore, rely on a reference state that also defines Al and O. This is provided by the Al(l) + α-Al$_2$O$_3$ reference which defines the most stable Al$_2$O$_3$. The conditions defined by the equilibrium between β-NiAl(O) and α-Al$_2$O$_3$ are significantly different from the reference state. Specifically, the Al$_2$O$_3$ in this case is in equilibrium with a significant $a(\text{Ni})$, a reduced $a(\text{Al})$ and a correspondingly increased $a^*(\text{O})$. This changed environment could result in either: 1) the dissolution of species in Al$_2$O$_3$, or 2) the introduction of an equilibrium concentration of structural defects, or a combination of both. The formation of oxide compounds and solution phases would reduce $a(\text{Al}_2\text{O}_3)$ as seen in the pseudo-binary systems: Cr$_2$O$_3$-Al$_2$O$_3$, Y$_2$O$_3$-Al$_2$O$_3$ and NiO-Al$_2$O$_3$. If Al$_2$O$_3$ remained closely stoichiometric, then an equilibrium concentration of structural defects corresponding to this changed environment could result in an increased reactivity and measured $a(\text{Al}_2\text{O}_3) > 1$. This is identical to the case discussed for $a^*(\text{O})$, where an $a(\text{Al}_2\text{O}_3) > 1$ simply result from the choice of a reference state that defines the most stable "defect free" Al$_2$O$_3$. While $a(\text{Al}_2\text{O}_3)$ is not expected to differ significantly from unity for case considered here, any variation in $a(\text{Al}_2\text{O}_3)$ will have a significant effect on $a^*(\text{O})$ at the alloy/scale interface according to the formation reaction of Al$_2$O$_3$, equation 12. This formation reaction must always hold and in these measurements no assumptions about the activities of Al, O or Al$_2$O$_3$ are needed.

$$2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 \qquad K_{12} = \frac{a(\text{Al}_2\text{O}_3)}{a(\text{Al})^2 a(\text{O})^3} \qquad [12]$$

From an experimental perspective it is not necessary to start with β-NiAl that is saturated with O or Al_2O_3 that is saturated with Ni. The low solubility limits of O and Ni means that both phases will saturate during the initial stages of the experiment allowing equilibrium to be quickly obtained. The interstitial nature of O in β-NiAl means that it is only important to get the correct concentration of the substitutional components observed at the alloy/scale interface. A further experimental consideration is that a unique reaction path develops for a given set of oxidation conditions (*i.e.*, bulk alloy composition, oxygen pressure and temperature). Therefore the alloy/scale composition changes with oxidation temperature as the transport kinetics in the alloy and scale change. In contrast, the measured $a(Al)_I$, $a(Ni)_I$, $a^*(O)_I$ and $a(Al_2O_3)_I$ at the β-NiAl(O)$_I$ + α-Al_2O_3 equilibrium are made at a fixed composition over a range of temperatures. Therefore to fully explore the thermodynamics of the alloy/scale interface a select number of alloys need to be measured that span the composition range observed at the interface during oxidation. To take full advantage of these results they need to be incorporated into a solution model that will allow accurate interpolation to all compositions.

CONCLUSIONS

The thermodynamic properties of the alloy and oxide compound at the alloy/scale interface define the driving force for solid-state transport in the alloy and oxide. A method was proposed that allows the thermodynamic properties of the alloy/scale interface to be determined directly. This method is based on the concept of local equilibrium and the alloy + scale equilibrium is assumed to very closely approximate the alloy/scale interface observed during steady-state oxidation. The thermodynamic properties of the alloy + scale equilibrium can be measured directly by the vapor pressure technique with a Knudsen effusion-cell mass spectrometer (*KEMS*) configured with a multiple effusion-cell vapor source. The example of β-NiAl(O) + α-Al_2O_3 was considered where $a(Al)_I$, $a(Ni)_I$, $a^*(O)_I$ and $a(Al_2O_3)_I$ can be determined by the systematic measurement of the relative partial pressures of Al(g), Al_2O(g) and Ni(g) in equilibrium the alloy in an α-Al_2O_3 effusion-cell combined with the use of pure Ni(s) and Al(l) + Al_2O_3(s) as the reference states. A systematic determination of these activities in alloy compositions that closely resemble those observed at the alloy/scale interfaces, together with a well characterized pre-oxidation process, will improve our understanding of how ternary and higher order alloy additions effect oxidation behavior.

ACKNOWLEDGEMENTS

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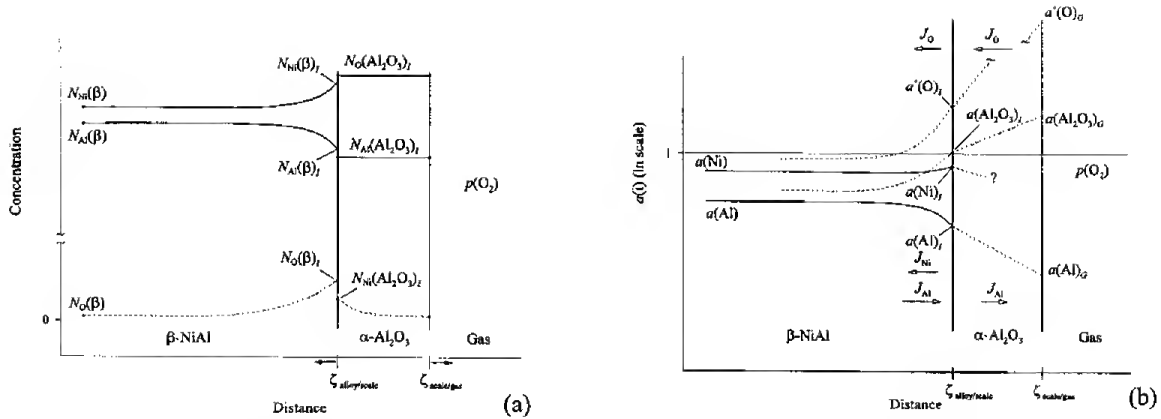20. D. J. Young, F. Gesmundo, *High Temperatures - High Pressures*, **20**, 1, (1988).

Figure 1. a) Schematic representation of the concentration profile of the oxidation of β-NiAl in pure oxygen. b) The corresponding representation of the thermodynamic activities of Ni, Al, O and Al_2O_3 across the interaction zone shown.

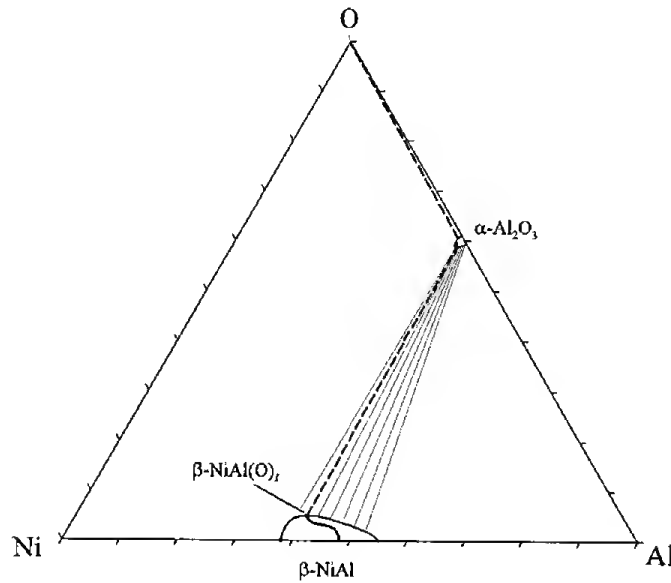Figure 2. Schematic isothermal section of the condensed phase diagram of the Ni-Al-O system showing the diffusion-path for steady-state oxidation of β-NiAl(O). The solubility of O in β-NiAl(O) and Ni in α-Al_2O_3 have been exaggerated. The identified tie-line represents the β-NiAl(O)$_I$ / α-Al_2O_3 interface.
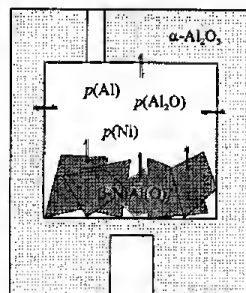
Figure 3. Schematic of an Al_2O_3 effusion-cell containing a β-NiAl(O)$_I$ sample.